

The Performance of Low Cost and Highly Energy Dense Hybrid Zinc|Manganese Dioxide-Copper Scaled-Cells

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Introduction & Objective

1. Zinc (Zn)-anode batteries are safe, non-flammable and contain cheap and abundant raw materials. Zn's theoretical 2e capacity is also high at 820mAh/g. Theoretically, when paired with a high-capacity cathode, it has the energy density to match or outperform lead acid and lithium-ion batteries.
2. It, however, lacks a cathode which also has a high theoretical capacity and can be cycled >1000 times at C-rates that are of interest for various applications like power backup or long duration storage.
3. In this presentation, we report the development of a new hybrid cathode design utilizing cheap and abundant manganese dioxide (MnO₂) and copper/copper oxide (CuO) mixture, which delivers ~280mAh/g and ~600mAh/g (weight of both active materials included) depending on the voltage range used for >1000 cycles.
4. The manufacturability of these cathodes is also studied where we report on cylindrical cells with a high capacity between ~6 and 16Ah, where the electrodes are produced on the line.
5. Our objective of making a cheap and manufacturable Zn-anode cell that competes with lithium-ion and lead acid batteries is the focus of this presentation.

Results

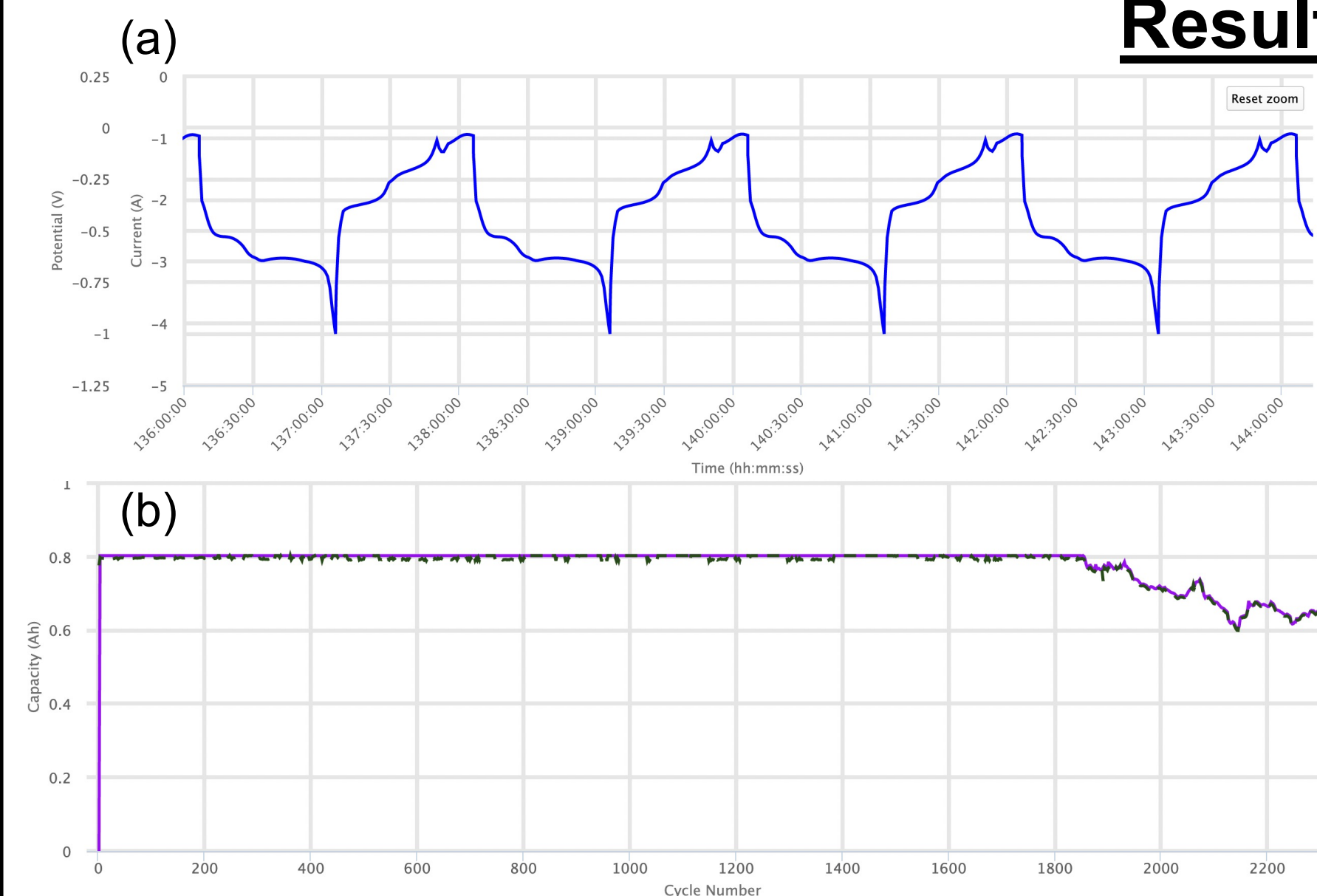


Figure 1. (a) Voltage versus time curve of the MnO₂ and Cu second electron half cell. (b) Charge and Discharge Capacity versus Cycle Number. This is a MnO₂ and Cu half-cell. Which exceeded 2300 cycles.

1. The hybrid cathodes tested in Figure 1 contained MnO₂, Cu and CNTs. There was no binder used as we had found in our previous work that binder affected the performance of MnO₂. These electrodes were cycled at 1C.
2. As shown in Figure 1, the curves displayed characteristic MnO₂ electrochemical reactions, where the flat plateau was due to its dissolution-precipitation reactions. However, some cuprous oxide reactions were also seen which was expected as Cu exhibited oxidation from Cu⁰ to Cu¹ to Cu² during charge. This was the first such demonstration of 2 raw materials- MnO₂ and Cu-that exhibited conversion reactions.
3. The capacity retention data in Figure 1b showed that this hybrid cathode was able to withstand conversion reactions that result in complete degradation and reformation of the crystal structure. The hybrid cathodes showed remarkable capacity retention to >2300 cycles.
4. However, these cathodes had CNTs as the source of carbon which are expensive. To make this truly manufacturable on a large scale we would need to replace CNTs with low cost graphite and add binder to the cathodes.

Manufacturable Electrodes

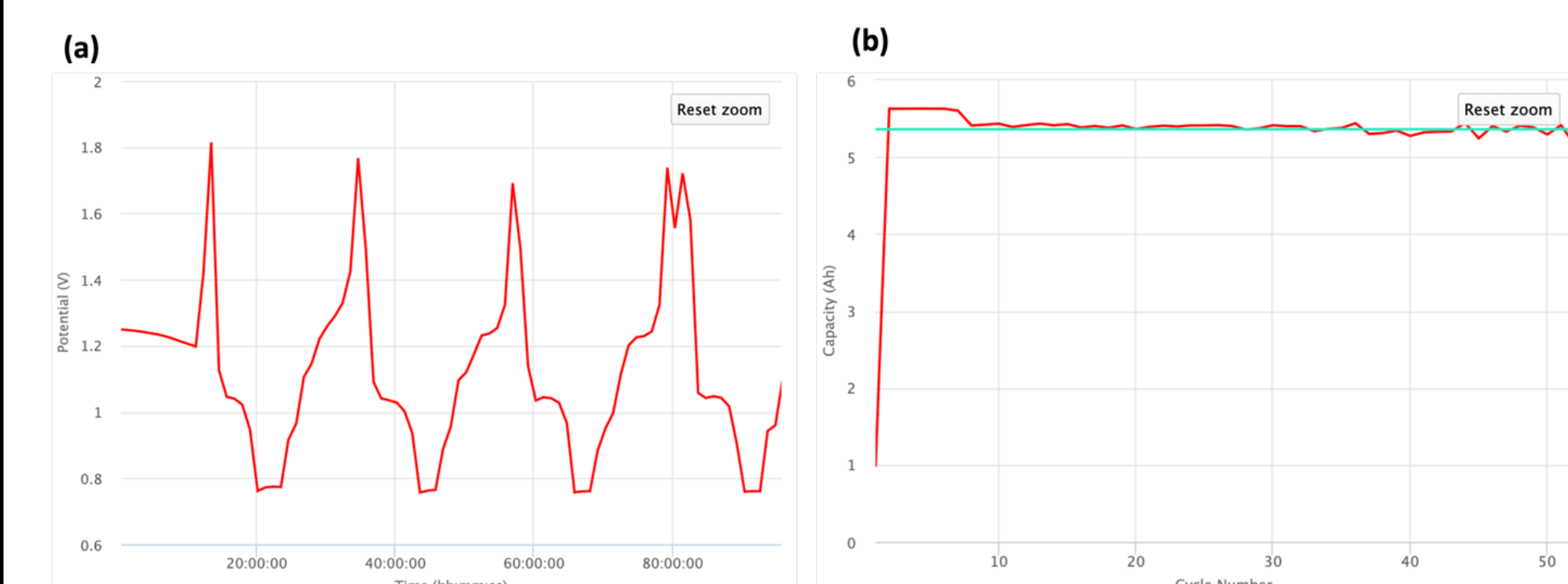


Figure 2. (a) Charge and discharge curves of a 5.36Ah full cell test containing graphite as the carbon source. (b) Capacity retention of the 5.36Ah full cell test.

1. We tested the manufacturability of our electrodes using Teflon binder and Graphites as a replacement for CNTs.
2. The electrodes were made using commercial manufacturable processes and the electrodes were also scaled in size and capacity to 5.36Ah as shown in Figure 2.
3. The electrodes showed excellent charge and discharge characteristics as shown in Figure 2a. They were able to retain their capacity and energy even in scaled sizes as shown in Figure 2b.

Manufacturability – Cylindrical Design

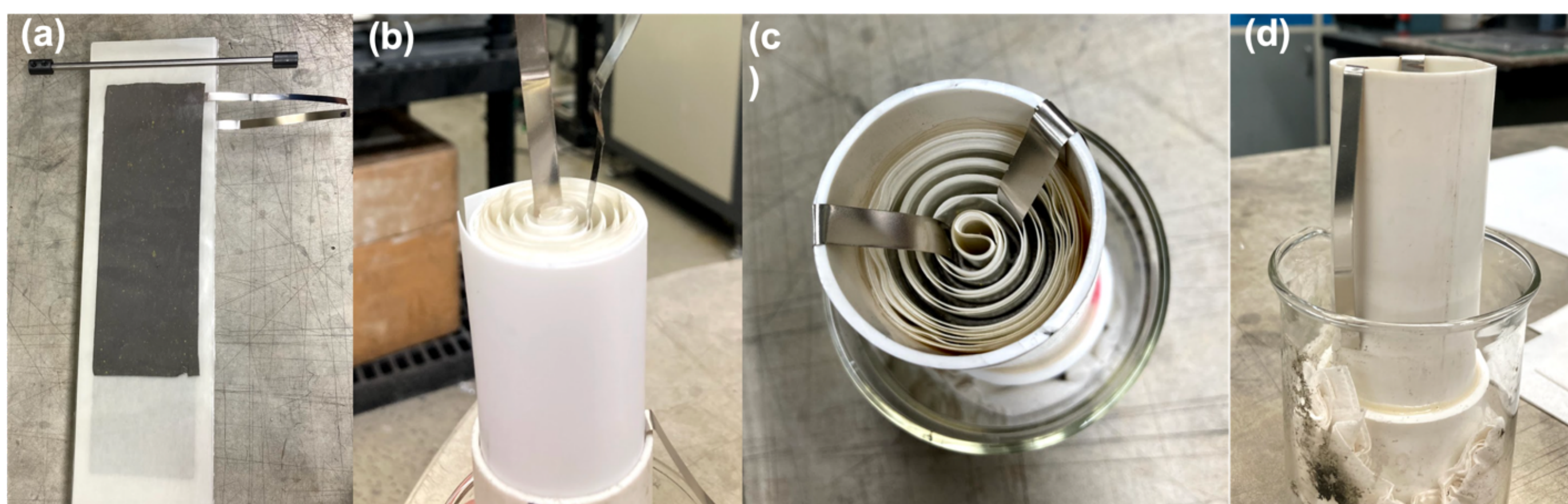


Figure 3. (a) Process of rolling electrodes into a jelly roll. (b) The jelly roll pack consisting of electrodes and separator. (c) Inserting the jelly roll pack into the cylindrical can. (d) The cylindrical can containing the hybrid cathode and Zn anode.

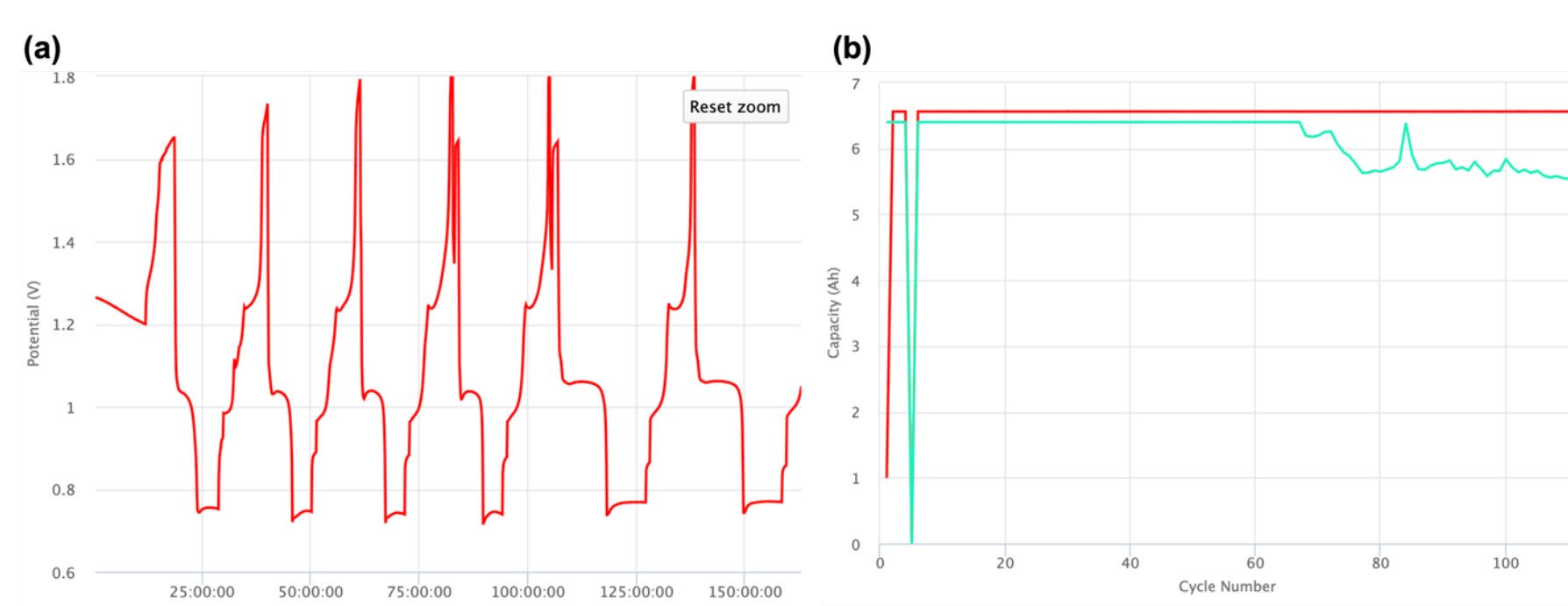


Figure 4. (a) Charge and discharge curves of a 6.5Ah cylindrical cell. (b) Capacity retention of a 6.5Ah cylindrical cell.

1. UEP has a roll-to-roll continuous manufacturing line setup at Pearl River. We are experts at continuous manufacturing of cylindrical cells of various sizes. Apart from ease of large-scale and continuous manufacturing cylindrical cells also offer other advantages like better compression of the jelly roll in a cylindrical can, ability to absorb internal pressure experienced by electrode expansion and contraction during cycling and better ability to increase the capacity of the cell by altering electrode length and thickness.
2. We built preliminary small cylindrical cells of 6.5Ah. The process of making these cells is shown in Figure 3. The electrodes can be made continuously and made into a jelly roll.
3. The charge and discharge performance of this cylindrical cell is shown in Figures 4a and b.
4. The charge and discharge curves are comparable to the prismatic cells shown in Figures 1 and 2. The hybrid cathodes performance are transferable to other form factors. This is the first such demonstration of a complete conversion battery in cylindrical form factor.
5. Most commercially manufactured cells exhibit only intercalation reactions like lithium-ion or proton intercalation in primary Zn-anode batteries. Being able to manufacture scalable cylindrical cells of these conversion electrodes opens the opportunities to build batteries of various formations that serve many applications.
6. The excellent coulombic efficiency and the capacity retention of the cells shown in Figure 5b indicate the long term reversibility of these hybrid cathodes when paired with Zn anodes.

Conclusions & Future Work

We have demonstrated a hybrid cathode made of cheap and abundant raw materials like MnO₂ and Cu or CuO that deliver between 280 to 600mAh/g for >2000 cycles. These hybrid cathodes electrochemically react through a conversion mechanism where they dissolve and precipitate to deliver their capacity. The pairing of this electrode with a conversion Zn-anode results in the formation of a full conversion battery.

We further demonstrated the manufacturability of these electrodes in cylindrical form factor and showed its excellent performance in scaled cylindrical cells. These cells can be made on a UEP commercial line, where we have perfected a continuous roll-to-roll manufacturing process. Many innovations during this project lead to the formation of this scaled cylindrical cell.

This cathode is a game changer for alkaline Zn-anode batteries as it can compete with lead acid and lithium-ion batteries in terms of energy density and cost. With improvements to the current collector material and changes to the formulation, we can make this conversion battery at ~50/kWh and cycle at various C-rate where high power or energy density are required. This is a very competitive battery capable of being a drop-in replacement for lead acid batteries for UPS and solar microgrid applications. Its high rate and energy performance makes this battery even applicable for electric bikes and long duration storage.

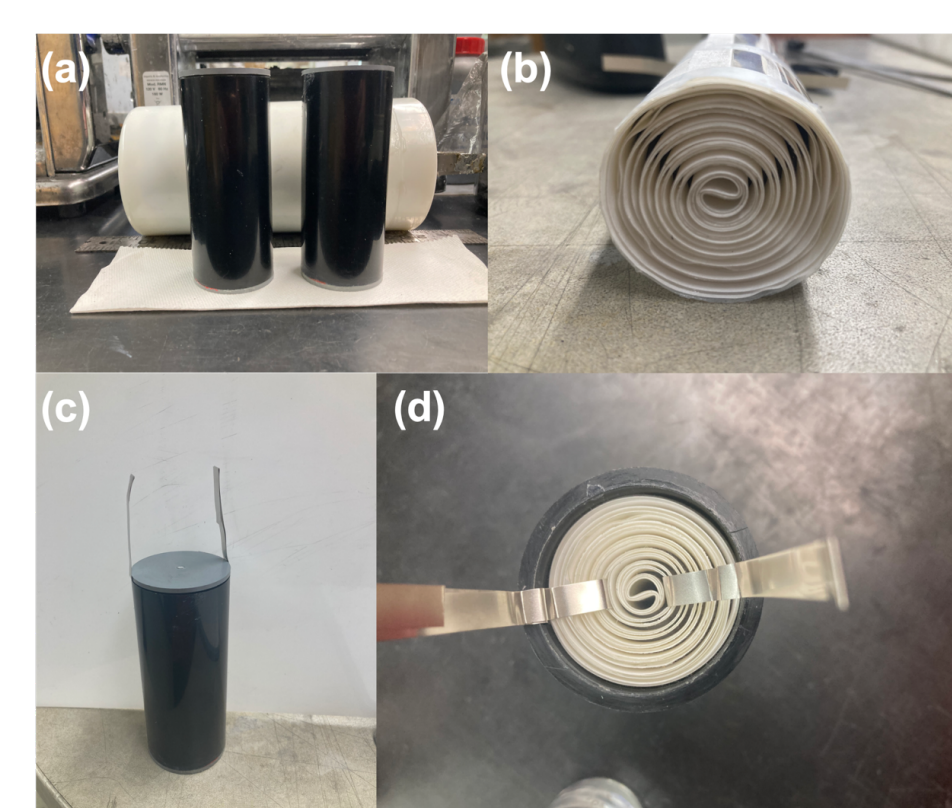


Figure 5. (a) Scaling the cylindrical cell capacity to 15.5Ah cell. (b) Jelly roll of a 15.5Ah cylindrical cell. (c) A 15.5Ah cylindrical cell. (d) A top-down view of a 15.5Ah cylindrical cell.

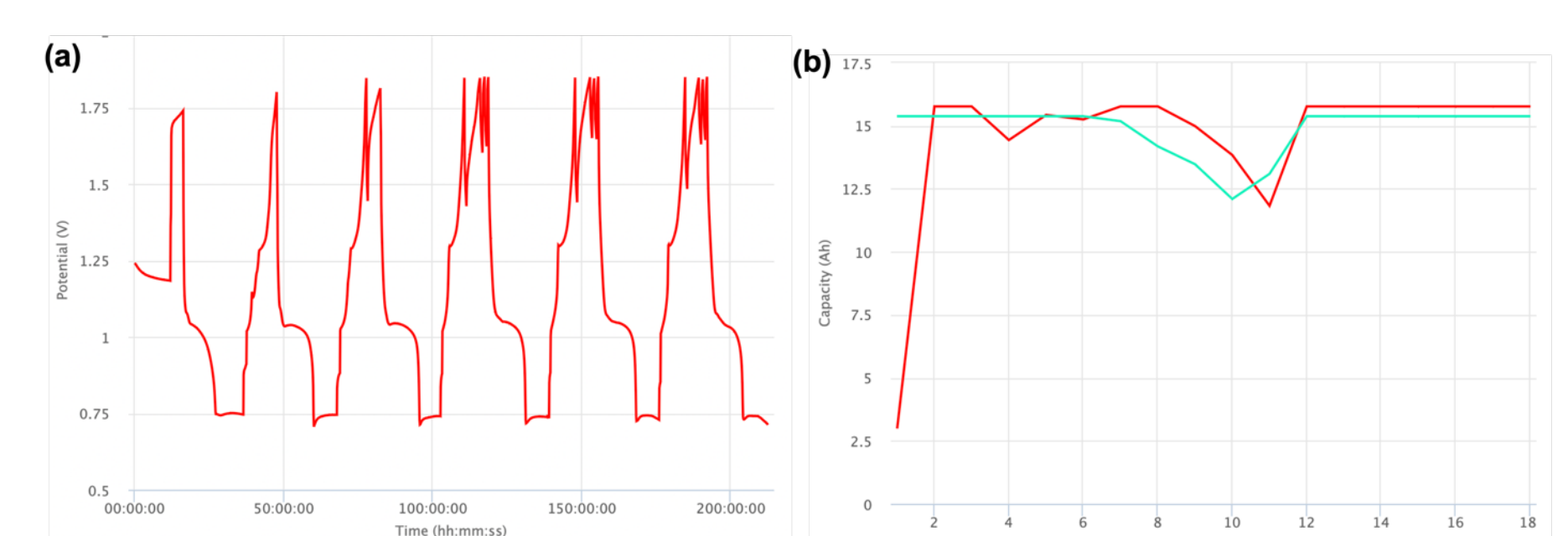


Figure 6. (a) Charge and discharge curves of a 15.5Ah cylindrical cell. (b) Capacity retention of a 15.5Ah cylindrical cell.

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